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14. ABSTRACT
We performed research on the design and realization of high performance substrates for surface enhanced Raman scattering (SERS), and elucidated the role of chemical interactions between analyte molecules and a plasmonic substrate, the so-called "chemical effect." Two approaches were taken for the realization of high performance SERS substrates. In the first, metal nanostructures supporting surface plasmons were fabricated by electron beam lithography. We demonstrated that by optimizing the design of metallic nanostructures, the average enhancement factor (EF) for surface-enhanced Raman scattering (SERS) could be as large as 8.4x10^8. The angular dependencies of the local field enhancement and the Raman emission enhancement were also investigated. We demonstrated that a stronger SERS signal resulted when the plasmonic substrate was illuminated with a collimated, rather than focused, laser beam. In the second approach, a pulsed laser was used to texture a silicon wafer to form sharp features. Silver was evaporated onto the wafer, and the resulting structures were found to exhibit very high SERS performance. In the theory effort, a comprehensive analysis of the chemical effect, including analytical and computational modeling, was accomplished.

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Final report for grant FA-9550-08-1-0285, "SERS engineering collaboration"
PI: Kenneth Crozier, Harvard University
June 2012

Thrust: optical antennas (Crozier)

(a) Accomplishments: We demonstrated that by optimizing the design of metallic nanostructures, the average enhancement factor (EF) for surface-enhanced Raman scattering (SERS) could be as large as 8.4×10^8. This was achieved by optimizing the shape of the nanostructures and arranging them in periodic array.

(b) Summary: SERS substrates were designed to support "double" surface plasmon resonances, i.e. at both excitation and Stokes frequencies [K5] (also see thesis (f)). These consisted of three layers: a nanoparticle array, a silicon oxide spacer, and a planar metallic film, as shown in Fig. 1(a). This multilayer structure combined localized surface plasmons on the nanoparticles with surface plasmon polaritons excited on the metallic film. The largest SERS enhancement factor for a gold device was measured to be 7.2×10^7, which was more than 2 orders of magnitude larger than that measured on a gold nanoparticle array on a glass substrate. The largest SERS enhancement for a silver device was measured to be 8.4×10^8.

The angular dependencies of the local field enhancement and the Raman emission enhancement were investigated for this double resonance SERS substrate. It was found that the local field enhancement was very sensitive to the incident angle [K10] (also see thesis (f)). We demonstrated that a stronger SERS signal resulted when the plasmonic substrate was illuminated with a collimated, rather than focused, laser beam.

The Raman emission enhancement was also found to have a strong angular dependence on the detection direction, with the substrate "beaming" the Raman emission so that different Raman lines havd different far-field patterns (see thesis (f)). Concentric ring gratings were also studied as a means to collimate Raman emission, as shown in Fig. 1(b). The collimated Raman emission can be effectively collected by objective lens with low numerical aperture [K7].

To achieve even larger EF for SERS, a top-down fabrication procedure was developed to lithographically fabricate pairs of nanoparticles separated by a controllable gap size that can be as small as 3 nm (Fig. 1(c)) [K8]. This could lead to large optical near field within the nanoscale gap. The EF for this SERS substrate was ~25 times larger than the structure with gap size of 12 nm.

Modifications to the shapes of the constituent optical antennas were also investigated to realize localized high electric and magnetic field enhancement [K4]. It was shown that a fan-rod electric antenna design combined the advantages of the rod antenna and the bowtie antenna, and had higher field enhancement than either. The performance of a loop shaped magnetic antenna consisting of a pair of metallic strips with offsets was also verified numerically, with high magnetic field enhancement being observed in the simulation. In both of the designs, the concepts of charge and current reservoirs contributed to high electric and magnetic field enhancement.

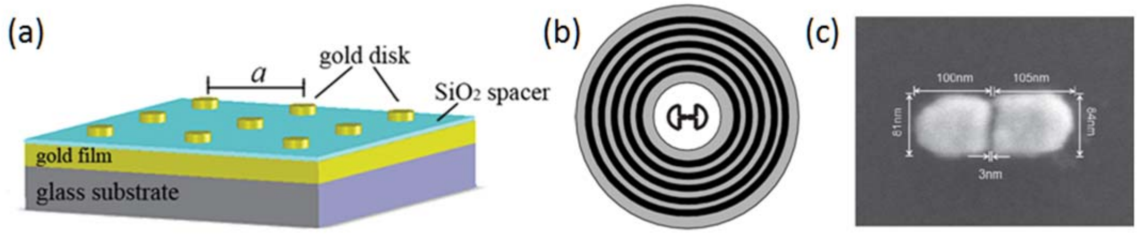

Figure 1: (a) SERS substrate that supports double plasmonic resonances. (b) Fan rod antenna structure placed at the center of concentric rings. (c) Nanorod dimer structure separated by a nanoscale gap with size of ~3 nm.

For SERS measurement, self-assembled monolayers of benzenethiol were formed on the gold nanostructures. This was performed by immersing the samples in a 3 mM solution of benzenethiol in ethanol for 2 hrs, rinsing with neat ethanol, and then blow drying with nitrogen.

The SERS measurements were carried out with a confocal Raman microscope (Horiba® LabSpec). The Raman signal was collected by an objective lens (20×, NA = 0.4) and input to a spectrometer containing a thermoelectrically-cooled CCD array. To determine the SERS enhancement factor, reference measurements were also made on a 500 μm thick sample cell containing a neat solution of benzenethiol.

(c) List of people: Mohamad G. Banaee, Yizhuo Chu, Dongxing Wang, Wenqi Zhu, Kenneth Crozier

(d) List of publications:

K1. " Experimental observation of narrow surface plasmon resonances in gold nanoparticle arrays," Yizhuo Chu, Ethan Schonbrun, Tian Yang and Kenneth B. Crozier, Applied Physics Letters vol. 93, 181108 (2008)

K2. " Experimental study of the interaction between localized and propagating surface plasmons," Yizhuo Chu and Kenneth B. Crozier, Optics Letters vol. 34, 244 (2009)

K3. "Gold nanorings as substrates for surface-enhanced Raman scattering," Mohamad G. Banaee and Kenneth B. Crozier, Optics Letters vol. 35, 760 (2010)

K4. "Charge and current reservoirs for electric and magnetic field enhancement," Dongxing Wang, Tian Yang, and Kenneth B. Crozier, Optics Express vol. 10, 10388 (2010)

K5. "Double-Resonance Plasmon Substrates for Surface-Enhanced Raman Scattering with Enhancement at Excitation and Stokes Frequencies," Yizhuo Chu, Mohamad G. Banaee and Kenneth B. Crozier, ACS Nano vol. 4, 2804 (2010)

K6. "Mixed Dimer Double-Resonance Substrates for Surface-Enhanced Raman Spectroscopy," Mohamad G. Banaee and Kenneth B. Crozier, ACS Nano vol. 5, 307 (2011)

K7. "Optical antennas integrated with concentric ring gratings: electric field enhancement and directional radiation," Dongxing Wang, Tian Yang, and Kenneth B. Crozier, Optics Express vol. 19, 2148 (2011)

K8. "Lithographically Fabricated Optical Antennas with Gaps Well Below 10 nm," Wenqi Zhu , Mohamad G. Banaee , Dongxing Wang , Yizhuo Chu , and Kenneth B. Crozier, Small vol. 7, pp. 1761-176 (2011);

K9. "Double resonance surface enhanced Raman scattering substrates: an intuitive coupled oscillator model ," Yizhuo Chu, Dongxing Wang, Wenqi Zhu, and Kenneth B. Crozier, Optics Express vol. 19, 14919 (2011);
K10. "Beamed Raman: directional excitation and emission enhancement in a plasmonic crystal double resonance SERS substrate ," Yizhuo Chu, Wenqi Zhu, Dongxing Wang and Kenneth B. Crozier, Optics Express vol. 19, pp. 20054-20068 (2011);
(f) List of theses: Yizhuo Chu, Harvard University, 2010. SERS substrate that supports double plasmonic resonances was studied in this thesis. Angular effect of Raman excitation and emission was also included in the thesis.

Thrust: theory (Aspuru-Guzik)

Summary

The theory part of the group elucidated the role of chemical interactions between analyte molecules and a plasmonic substrate in the surface-enhanced Raman response, the so-called "chemical effect." A comprehensive analysis of the chemical effect, including analytical and computational modeling, and also comparison with experiments, has been accomplished. As an extension to the originally proposed milestone, the chemical effect in a non-linear SERS setup, coherent anti-Stokes Raman scattering (CARS), has been explored. The results of the studies were published in 10 papers and one more manuscript has been submitted for publication. One graduate student, Roberto Olivares-Amaya, have received PhD with the thesis titled: "Quantum Chemistry in Nanoscale Environments: Insights on Surface-Enhanced Raman Scattering and Organic Photovoltaics."

Analytical model: A many-body model of SERS that provides a unified description for both electromagnetic and chemical effects has been developed. Within the model the quantum plasmon modes were introduced following the works of Bohm and Pines, while the coupling between the metal and molecules was described by an electron tunneling term. Then the interaction between the plasmon modes in the metal and electronic excitations the molecule can be considered as a Forster energy transfer that contributes to the conventional electromagnetic enhancement, and also plasmon assisted charge-transfer excitation which corresponds to the chemical effect. This model helped us with qualitative understanding of computational results.

Cluster model: A cluster model has been utilized for the computational analysis of chemical effects in SERS. The model is based on the assumption that the chemical effects are spatially local. Within the model a structure of an analyte molecule adsorbed on a small Au or Ag cluster has been optimized and electronic and Raman responses of the complexes were computed. The computations were accomplished using time-dependent density functional theory (TDDFT) as implemented in Turbomole quantum chemistry package and using home-made post processing codes. The results and the details of the model were described in Refs. [A1, A2, A5, A6]. As compared to previous works our model allowed for calculations of: frequency dependent Raman responses; Raman responses close to electronic resonance excitations; surface-enhanced CARS. The main effects of chemical bonding between analyte molecules and the substrate can be characterized as: off-resonance (a proximity to the surface and orientation relative to the surface) and resonance (formation of metal-molecular states). According to our estimations, the off-resonance effects can give about 10 times enhancement of the Raman signal, and the resonance effects give about 100-1000 time enhancement. These factors, together with electromagnetic enhancement due to the plasmon mode, enter multiplicatively into the total enhancement of Raman signal. While the direct comparison of the computed enhancement factors with experimental data is complicated, our group was able to associate the chemical effects with modifications of Raman spectra of analyte molecules, specifically shifts of the Raman lines and changes of peak intensities. It has been demonstrated that these spectra modifications can be efficiently described using a metal-molecule cluster model [A2]. The use of mixed metal substrates was proposed to improve the control of the chemical effect with analytes that do not bind well to plasmonic materials. An enhancement was observed using Pd or Pt with Ag clusters. We termed this effect a "lending SERS", as the dopant metal is contributing to SERS. This effect was also shown to exist experimentally, although there needs to be a further characterization of the surface [A11].

Resonance Raman model: A simplified sum-over-states scheme for computing Raman spectra and Raman excitation profiles has been introduced [A5]. The proposed sum-over-states approach uses derivatives of electronic excitation energies and transition dipole moments, which can be efficiently computed from TDDFT. The resonance Raman spectra and Raman excitation profiles of nucleic acid bases have been analyzed. Our work emphasizes the intricate interplay between the contributions of the excited-state gradients (Albrecht A terms) and contributions stemming from derivatives of transition dipole moments (Albrecht B terms) in determining resonance Raman cross sections. The A terms are dominant in the strictly resonant case, while the B terms determine the Raman cross sections in the non-resonant limit. By using both terms, the proposed method can treat the resonant and non-resonant cases on equal footing. Resonance Raman spectra and Raman excitation profiles of nucleosides have been predicted and compare well with available experimental resonance Raman data. The major source of error seems to be in electronic excitation energies, which are can be off by up to 0.5 eV with TDDFT. Our results provide a theoretical foundation for the understanding of the chemical effect in SERS, which can be interpreted as resonance enhancement due to metal--molecule interfacial states.

Quantum chemistry in a electrostatic environment: A novel approach to the molecular electronic structure in arbitrary electrostatic environments that is compatible with standard quantum chemical methods and can be applied to medium-sized and large molecules have been developed and implemented [A4, A8]. The scheme denoted CheESE (chemistry in electrostatic environments) is based on the description of molecular electronic structure subject to a boundary condition on the system/environment interface. Thus, it is particularly suited to study molecules on metallic surfaces. We present the theory, implementation, and application of a simple, electrostatics-based approach for a specific class of multi-scale problems involving molecules at metallic interfaces of arbitrary shape. The proposed model is capable of describing both electrostatic effects near nanostructured metallic surfaces and image-charge effects. We present an implementation of the CheESE model using Gaussian basis sets and thus useable in conjunction with standard quantum chemical software packages. We derive the working equations for a a specific case DFT calculations using the CheESE model. A particular emphasis is on an efficient computation of the interaction potential and the associated matrix elements in a Gaussian basis set. We apply the method to study environment effects on the electronic structure of molecules both between grounded metal plates and under external bias. The effects of the external field and of the mutual polarization are explored for a neutral quadrupolar molecule (benzene), a neutral dipolar molecule (glycine zwitterion), and a charged molecule (benzene anion), making a detailed comparison with the simpler picture of a static external field, which is not solved self-consistently. The difference, which we term `the image charge effect', is found to strongly depend on the multipole character of the system's total charge distribution. Thus, it is quite small in the charge-neutral, quadrupolar, benzene system, but somewhat larger in the dipolar (zwitterionic) glycine case. Similarly, it is quite significant in the charged benzene anion, where it modifies the total molecular energy by between 1 and 20 kcal/mol, which is comparable in size to the changes induced by a static field of strength 1 V/Angstrom. As a result, we found that the benzene anion can actually be stabilized relative to neutral benzene when confined inside a grounded cavity.

SECARS: The prospects of realizing a surface enhanced CARS experiment were evaluated by developing code to predict CARS with density functional theory (DFT). Approximations to the CARS signal based on the response properties of DFT were developed [A6], and molecular spectra were simulated on and off slab models of a metal surface. The presence of a silver surface was predicted to chemically enhance the intensity of CARS scattering by a factor on the order of 10. The ability of this theoretical methodology to predict the absolute value of a CARS cross-section was evaluated through an experimental collaboration [A7]. CARS susceptibilities of liquid benzenethiol were computationally reproduced in that study within an order-of-magnitude, with the correct polarization dependence. These preliminary results motivate the further pursuit of surface enhanced CARS experiments which might at significant enough intensities be even more intensely enhanced than conventional Raman spectroscopy.

List of publications:

A11. Roberto Olivares-Amaya, Dmitrij Rappoport, Philip Munoz, Paul Peng, Eric Mazur and Alán Aspuru-Guzik. **Can Mixed-Metal Surfaces Provide an Additional Enhancement to SERS?** preprint (2012).

A10. John Parkhill, David G. Tempel and Alán Aspuru-Guzik. **Exciton Coherence Lifetimes from Electronic Structure**. *Journal of Chemical Physics* 136, no. 10 (March 2012): 104510.

A9. Roshan L. Aggarwal, Lewis W. Farrar, Semion K. Saikin, Xavier Andrade, Alán Aspuru-Guzik, and Dennis L. Polla. **Measurement of the Absolute Raman Cross Section of the Optical Phonons in Type Ia Natural Diamond**. *Solid State Communications* 152, no. 3 (February 2012): 204–209.

A8. Mark A. Watson, Dmitrij Rappoport, Elizabeth M. Y. Lee, Roberto Olivares-Amaya, and Alán Aspuru-Guzik. **Electronic Structure Calculations in Arbitrary Electrostatic Environments**. *The Journal of Chemical Physics* 136, no. 2 (January 9, 2012): 024101.

A7. Roshan L. Aggarwal, Lewis W. Farrar, John Parkhill, Alán Aspuru-Guzik, and Dennis L. Polla. **Measurement of the Third-order Nonlinear Optical Susceptibility X(3) for the 1002-cm-1 Mode of Benzenethiol Using Coherent anti-Stokes Raman Scattering with Continuous-wave Diode Lasers**. *Journal of Raman Spectroscopy, Early View* (November 2011).

A6. John A. Parkhill, Dmitrij Rappoport, and Alán Aspuru-Guzik. **Modeling Coherent Anti-Stokes Raman Scattering with Time-Dependent Density Functional Theory: Vacuum and Surface Enhancement**. *The Journal of Physical Chemistry Letters* 2, no. 15 (August 4, 2011): 1849–1854.

A5. Dmitrij Rappoport, Sangwoo Shim, and Alán Aspuru-Guzik. **Simplified Sum-Over-States Approach for Predicting Resonance Raman Spectra. Application to Nucleic Acid Bases**. *The Journal of Physical Chemistry Letters* 2, no. 11 (June 2, 2011): 1254–1260.

A4. Roberto Olivares-Amaya, Michael Stopa, Xavier Andrade, Mark A. Watson, and Alán Aspuru-Guzik. **Anion Stabilization in Electrostatic Environments**. *The Journal of Physical Chemistry Letters* 2, no. 7 (April 7, 2011): 682–688.

A3. Roshan L. Aggarwal, Lewis W. Farrar, Semion K. Saikin, Alán Aspuru-Guzik, Michael Stopa, and Dennis L. Polla. **Measurement of the Absolute Raman Cross Section of the Optical Phonon in Silicon**. *Solid State Communications* 151, no. 7 (April 2011): 553–556

A2. Semion K. Saikin, Yizhuo Chu, Dmitrij Rappoport, Kenneth B. Crozier, and Alán Aspuru-Guzik. **Separation of Electromagnetic and Chemical Contributions to Surface-Enhanced Raman Spectra on Nanoengineered Plasmonic Substrates**. *The Journal of Physical Chemistry Letters* 1, no. 18 (September 16, 2010): 2740–2746.

A1. Semion K. Saikin, Roberto Olivares-Amaya, Dmitrij Rappoport, Michael Stopa, and Alán Aspuru-Guzik. **On the Chemical Bonding Effects in the Raman Response: Benzenethiol Adsorbed on Silver Clusters**. *Physical Chemistry Chemical Physics* 11, no. 41 (August 26, 2009): 9401.

Supported people:

Alán Aspuru-Guzik, Professor
Roberto Olivares-Amaya, Graduate Student
Sangwoo Shim, Graduate Student
John Parkhill, postdoc
Dmitrij Rappoport, postdoc
Semion Saikin, research associate
Michael Stopa, senior research scientist

Thesis:

Roberto Olivares-Amaya, "Quantum Chemistry in Nanoscale Environments: Insights on Surface-Enhanced Raman Scattering and Organic Photovoltaics."
The thesis will be available through the Harvard digital access system Dash.harvard.edu.

Thrust: SERS substrates produced by femtosecond laser techniques (Mazur)

We developed large area, planar, silicon-based SERS substrates using femtosecond laser nanostructuring. The substrates exhibited SERS enhancement factors of approximately 2x 10^7 at an excitation wavelength of 632.8 nm.

All substrates were fabricated using a femtosecond laser structuring process on an n-type silicon (100) wafer. A pulse train from a regeneratively amplified titanium:sapphire laser was used to generate 800-nm center wavelength, 100-fs pulses at a repetition rate of 1 kHz. This pulse train was frequency-doubled to a center wavelength of 400 nm using a thin BiBO3 crystal. The second harmonic pulse width exiting the crystal was less than 200 fs in duration. These laser pulses were loosely focused with a plano-convex lens to achieve an average fluence of 10 kJ/m^2 at the surface of a silicon wafer fastened to the inside of a 10 mm deep cuvette filled with deionized water. The cuvette was mounted on a computer-controlled two-axis translation stage and rastered at an appropriate speed such that each point on the silicon wafer was subjected to approximately 500 pulses. Laser ablation of Si resulted in a roughened substrate surface comprised of a quasi-ordered array of cones with an average period of 500 nm.

We coated the substrate with an 80 nm layer of silver via thermal evaporation. The rough surface acted as a physical catalyst for silver particle formation via Volmer-Weber growth, forming a dense layer of connected metal nanoparticles. The nanoparticles were highly uniform, with sizes ranging from 50-100 nm. The pristine silver surfaces were then functionalized with a self-assembled monolayer (SAM) of benzenethiol or mercaptobenzoic acid. These analytes were chosen as they are nonresonant with the Raman excitation sources used in this work, and readily form uniform SAMs on clean silver surfaces.

The performance of the resulting SERS substrates was characterized by comparison of the Raman spectra of adsorbed molecules relative to the pure analyte in solution. Using a 5 mW, s-polarized 632.8 nm HeNe laser, spectra were recorded through a 10× microscope objective (0.25 NA) and projected onto a thermoelectrically cooled charge-coupled device (CCD) array using a 1200 mm^{-1} diffraction grating. Individual spectra were recorded from both single spots (1.6 μm diameter) on the substrate, and from a 500 μm thick cell of neat benzenethiol for normalization. Relative to the neat cell, the average SERS cross-section is enhanced by a factor of $2x10^7$ for the 1572 cm^{-1} normal mode. These substrates offered a spatially uniform and large ($>10^6$) average SERS enhancement factor under excitation over the visible and near-infrared spectral regions.

Some sites exhibit extraordinary SERS enhancement ($>10^9$). This extremely small fraction of sites (hotspots) contributes a large percentage of the total Raman signal measured. We developed a process to isolate these sites to improve the SERS response: the substrate was coated in positive-tone photoresist, which prevented analyte molecules from adsorbing to the silver surface of the SERS substrate. We used galvanometric scan mirrors to subject each point on the substrate to 100 pulses from a regeneratively amplified titanium:sapphire femtosecond laser system (τ = 60 fs, λ_{center} = 795 nm, 100-kHz repetition rate). The laser pulses were focused by a single lens placed before the scan mirrors to achieve fluences at the substrate in the range 0-400 J/m^2. After fs-laser exposure, a commercial aqueous alkaline developer was used to remove the exposed photoresist covering the hot spots. This process of hotspot isolation (HSI) was shown to further enhance the SERS cross section by a factor of 27.

Further efforts focused on improving the chemical-electronic component of the SERS enhancement. We introduced a thin layer of a Pt-group metal on top of the majority Ag layer, with the intent of improving chemical binding without impacting the electromagnetic response. The goal was to utilize the high local fields of a Raman-active substrate when analyte molecules were strongly bound to the inactive overlayer. These mixed-metal substrates were produced by depositing a 2-5 nm layer of Pt on top of previously studied Ag SERS substrates. We studied SERS enhancement of 1,2-bis(4-pyridyl)ethylene (BPE), which binds strongly to platinum-group metals. In silver substrates with a 2 nm Pt overlayer, we observed a 2.5X enhancement in SERS response relative to bare Ag substrates. This effect was predicted by time-dependent density functional theory (TDDFT). The Raman signal was quenched for substrates with thicker Pt overlayers.

We also demonstrated increased SERS response from substrates using co-deposited Au-Ag alloys. By varying the ratio of Ag to Au, we optimized the enhancement due to the alloyed noble metal layer; for the Raman peak of BPE at 1200 cm^{-1}, a 1:2 Ag-Au alloy performs 5X better than the pure Ag substrate. These structures exhibited much finer surface roughness than pure Au or Ag substrates, which may explain the enhanced signal.

Both mixed-metal and alloy approaches contributed a chemical-electronic enhancement beyond the previously demonstrated electromagnetic enhancement. In particular, this chemical enhancement is expected to be specific to the analyte molecule, and is dependent on the composition of both the transition metal overlayer as well as the underlying noble metal.

Major Conclusions:

- We developed a Si-based SERS substrate using femtosecond lasers in a two-step process.
- The substrates show enhancement by a factor of $2x10^7$ relative to pure benzenethiol.
- The enhancement is highly uniform over large areas (cm^2).
- Some regions exhibit dramatically higher SERS enhancement. These hotspots can be isolated to produce a substrate with an enhancement factor of 10^9.
- Additional metal coating can selectively enhance chemical binding for certain analytes, further improving the enhancement factor.

Personnel: Eric Diebold, Paul Peng, Phil Munoz

Publications:

E1. "Femtosecond Laser-Nanostructured Substrates for Surface-Enhanced Raman Scattering" Diebold, E. D.; Mack, N.H.; Doorn, S. K; Mazur, E. *Langmuir* **2009**, 25, 1790-1794

E2. "Isolating Surface-Enhanced Raman Scattering Hot Spots Using Multiphoton Lithography" Diebold, E. D.; Peng, P.; Mazur, E. *J. Am. Chem. Soc.* **2009**, 131, 16357

Thesis: "Plasmon-enhanced nonlinear optics for applications in sensing and biology" Diebold, E. D. **2010**